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Optimization of the Adsorptive Dehydration of Ethanol –Water System

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Abstract
This work has explored the use of enzyme modified corn starch for the dehydration of ethanol – water mixtures. The X - RD analysis revealed that the enzyme modified corn starch is amorphous in nature while the Scanning Electron Microscopy revealed that the enzyme modified corn starch particles are spherical and irregular in shape with the existence of pores in the starch molecule. Optimization and modelling of the process variables was carried out using the RSM (BBD) design of experiment. The optimum process variables obtained were 2.75mm, 61.69min, and 49.99^{o}C for particle size, time, and temperature respectively at an initial concentration of 90wt% with predicted value of 95.4065wt%. The model was validated at the optimum conditions which gave an experimental value of 95.00wt% ethanol concentration. The experimentally result obtained is 99.574% close to the result obtained from the predicted optimum value.
Keywords: Response surface methodology, Enzyme Modified Corn starch, X – RD, SEM, Optimization, Ethanol – water mixtures, Box – Behnken design.

Introduction

Bio-ethanol is mainly produced through the fermentation of any sugar, starch or cellulose containing biomaterial (Frolkova and Raeva, 2010; Kumar et al., 2010). Fermentation of biomass produces a mixture containing 8-12% v/v ethanol mixed with water and some other organics (Sun et al., 2002). Despite being totally compatible with gasoline, anhydrous ethanol could be drawn out when in contact with water and form two separate phases (Kumar et al., 2010). Therefore, the presence of water in ethanol is undesirable when blending with hydrocarbons. Consequently, there is a great interest to dehydrate ethanol in order to use it as a fuel admixture (Frolkova and Raeva, 2010). However, separation of ethanol from a large amount of water is an energy intensive process. In lieu of this, alternative separation processes with energy saving potential have attracted attention; for example the development of pressure swing and thermal swing adsorption processes. The use of starch biomass in the dehydration of ethanol – water mixture is also being explored (Okewale et al., 2011; Okewale et al., 2013). The starch based adsorbents adsorb water by forming hydrogen bond between the hydroxyl groups on the surface of the adsorbents and the water molecules (Beery and Ladisch, 2001; Okewale et al., 2013). These materials are starch based adsorbents with high level of amylopectin. Another class of adsorbents, such as wheat straw and wood chips, is derived from cellulosic-based materials. These materials use xylans and cellulose as the major adsorbing mechanism instead of amylopectin (Mya, 2011).

The enzyme modified corn starch that is made use of in this work is more cost effective and less energy consuming compared to the other conventional materials that has been employed in ethanol – water separation. Modelling and optimization has been noted to be the most important stages in biological process, this is because it leads to system improvement and increases the efficiency of the process without increasing the cost (Bas and Boyaci, 2007). Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of engineering problems in which a response of interest is influenced by several variables (Montgomery, 2001). It is a technique for designing experiments building numerical models, evaluating the effects of variables and searching for the optimum combinations of factors. This method is more practical compared to the conventional 'one variable at –a- time' approaches as it arises from an experimental methodology which includes interactive effects among the variables and, eventually, it depicts the overall effects of the parameters on the process (Bas and Boyaci, 2007). RSM usually contains the following stages; (i) Design of a series of experiments for adequate and reliable measurement of the response of interest, (ii) Developing a mathematical model of the second order response surface with the best fittings through regression, (iii) Finding the optimal set of experimental parameters that produce a maximum or minimum value of response, (iv) Representing the direct and interactive effects of process parameters through two and three dimensional plots (Raissi, 2009). Box-Behnken has proposed some three level designs for fitting response surfaces (Box and Behnken, 1960). It requires an experiment number according to; $N = K^2 + K + C_p$, where, (K) is the factor number and C_p is the replicate number of the central point. These designs are formed by combining 2^K factorials with

incomplete block designs (Evans, 2003).

Box-Behnken design is a spherical, revolving design, viewed as a cube and consists of a central point and the middle point of the edges. The resulting designs are usually very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable. This means that the variance of the predicted response is the same at all points. Rotatability is a reasonable basis for the selection of response surface design (Deeng et al, 2004).

The objective of the work was to model the dehydration of ethanol –water mixtures using RSM (Box – Behnken Design), and optimization of the process variables as it affects the dehydration process.

Materials and Method

Native corn starch was procured from Eke – Awka market, Awka, Anambra Sate, Nigeria. It was sun dried and thermally treated in an oven at 110^{o}C for 16hours and thereafter classified into the desired particle size. Analytical grade of ethanol, de – ionized water, α – amylase, sodium azide, sodium phosphate, sodium chloride, and sodium hydroxide were purchased from accredited chemical dealers in Onitsha, Anambra State, Nigeria using a scale with an accuracy of 0.01g. The method of (Beery et al., 1998) was used for the enzyme modification of the corn starch. Ethanol – water mixture is prepared at the required mass concentrations of 90wt% ethanol. The fluid phase concentration was measured with the aid of an Abbé refractometer with automatic calibration in the experimental range of concentration.

Experimental Procedure

5g of the EMCOS biomass of a particular particle size was placed inside the 250ml conical flask in contact with 50ml of ethanol solution of a well-defined initial concentration (90wt%). The flask was corked and properly labeled.

The flasks were corked and left to stand in the thermostated water bath with an accuracy of ± 0.1^{o}C in the laboratory for 1hr and gently shaken, after which the end concentration of liquid was determined from the predetermined calibration graph using refractometry method.

Table1 Box-Behnken response surface methodology design of experiment for optimization of ethanol-water mixtures on adsorbents produced.

Run	Constants Coded values	Process duration (min) Coded values	Particle size (mm) Coded values	Temperature (^{o}C) Coded values
1	1	- 1	- 1	0
2	1	- 1	1	0
3	1	1	- 1	0
4	1	1	1	0
5	1	- 1	0	- 1
6	1	- 1	0	1
7	1	1	0	- 1
8	1	1	0	1
9	1	0	- 1	- 1
10	1	0	- 1	1
11	1	0	1	- 1
12	1	0	1	1
13	1	0	0	0
14	1	0	0	0
15	1	0	0	0
16	1	0	0	0
17	1	0	0	0
18	1	0	0	0

Table 2 Factor levels of independent variables for Box-Behnken design

Independent Variables	Low level (-1)	Mid - point (0)	High level (+1)
Process duration (min), X_1	20	50	80
Particle size (mm), X_2	2	3	4
Temperature (^{o}C), X_3	35	42.5	50

The matrix plan for Box Behnken's design with six replications at the centre is shown below;
Table 3 Box – Behnken Response Surface Design Matrix

No	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2
1	1	- 1	- 1	0	1	0	0	1	1	0
2	1	- 1	1	0	-1	0	0	1	1	0
3	1	1	- 1	0	-1	0	0	1	1	0
4	1	1	1	0	1	0	0	1	1	0
5	1	- 1	0	- 1	0	1	0	1	0	1
6	1	- 1	0	1	0	-1	0	1	0	1
7	1	1	0	- 1	0	-1	0	1	0	1
8	1	1	0	1	0	1	0	1	0	1
9	1	0	- 1	- 1	0	0	1	0	1	1
10	1	0	- 1	1	0	0	-1	0	1	1
11	1	0	1	- 1	0	0	-1	0	1	1
12	1	0	1	1	0	0	1	0	1	1
13	1	0	0	0	0	0	0	0	0	0
14	1	0	0	0	0	0	0	0	0	0
15	1	0	0	0	0	0	0	0	0	0
16	1	0	0	0	0	0	0	0	0	0
17	1	0	0	0	0	0	0	0	0	0
18	1	0	0	0	0	0	0	0	0	0

For three factor inputs of x_1, x_2 and x_3, the equation of the quadratic response is given as;

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

Characterization of the Corn Starch

Starch content determination

The starch content was determined using the method of Okewale et al., (2013).

Determination of pH

The pH was determined using standard test ASTMD 3828 – 80 (ASTM, 1996).

Determination of surface area

The specific surface area of the adsorbents was estimated using Sear's method (Al-Qadah and Shawabkah, 2009 and Alzaydien, 2009) by agitating 1.5g of the adsorbents samples in 100ml of diluted hydrochloric acid at a pH = 3. Then, 30g of sodium chloride was added while stirring the suspension and then the volume was made up to 150ml with deionized water. The solution was titrated with 0.1N NaOH to raise the pH from 4 to 9 and the volume, (V) recorded. The surface area according to this method was calculated as

$S = 32V – 25$. Where, S = surface area of the adsorbents, V = volume of sodium hydroxide required to raise the pH of the sample from 4 to 9.

Moisture content determination

The moisture content of the starchy adsorbents was determined using standard test ASTMD 2867 – 91 (ASTM, 1991).

Determination of bulk density

The bulk density was determined using the method of Okewale et al., (2013).

X – Ray Diffractometry (X – RD) analysis

The amorphous and crystallinity nature of the adsorbents was examined using a diffractometer system (EMPYREAN) using radiation Cuα (α1 = 1.540598Ao and α1= 1.544426Ao) and a secondary graphite monochromator (No), angle 2θ swept and the scan range (-0.002 – 74.99997°).

Scanning Electron Microscopy (SEM)

The surface morphology of the solid adsorbents was inspected using a scanning electron microscope (SEM) PHENOMWORLD operating at 25kV. Micro-particles for SEM studies were mounted on metal stubs with double – side adhesive, and coated with gold in vacuum using an IB – 3ion coater. The analysis also includes the micro pore size and diameter of the biomass.

Modeling and Optimization

The MATLAB software (R2008a) was used to model the BBD experimental runs while Design – Expert 8.03 software was used for the optimization of the process variables.

The Box – Behnken design was constructed as shown in the table 1 and the experiments run accordingly. The natural and coded values of independent variables are shown in table 2. The responses, Y which are the concentration of ethanol – water mixtures were determined. The coefficients of the RSM model matrix plan were

obtained with the equation (1.0).

$b = (F^TF)^{-1}F^TY = CF^TY$ (2.0)

Where F is response surface matrix plan.

If all the variables are assumed to be measureable, the response surface can be expressed as follows:

$y= f(x_1, x_2 \ldots x_k)$ (3.0)

The goal is to optimize the response variable y. It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. Usually, second order model is utilized in response surface methodology.

$$y = \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k} b_{ij} x_i x_j + \varepsilon \quad (4.0)$$

where ε is a random error. The 'b' coefficients, which should be determined in the second-order model, are obtained by the least square method. In general, the equation above can be written in matrix form;

$Y = bX + \varepsilon$ (5.0)

Where Y is defined to be a matrix of measured values, X to be a matrix of independent variables. The matrix b and ε consist of coefficients and errors, respectively. The solution of equation 5.0 can be obtained by matrix approach.

$b = (X^T X)^{-1} X^T Y$ (6.0)

where X^T is the transpose of the matrix X and $(X^T X)^{-1}$ is the inverse of the matrix $X^T X$.

The mathematical models were evaluated for each response by means of multiple linear regression analysis (Raissi, 2009). Maximization of the polynomials thus fitted was performed by desirability function method.

Results and Discussion

Characteristics of the EMCOS

The physico – chemical properties of the enzyme modified corn starch is shown in Table 1.0.

Table 4 Physico-chemical properties of Enzyme Modified Corn Starch (EMCOS)

Properties	Modified corn starch (EMCOS)
pH	6.0
Moisture content (%)	3.04
Colour	White
Starch content (%)	86.5
Bulk density (g/ml)	1.57
Micro pore volume (m^3/g)	0.2
Diameter (μm)	7.99
Oxygen (%)	86.6
Carbon (%)	13.4
Surface area (m^2/g)	200

Table 5 Summary Result of the Box – Behnken's Surface Response Methodology

No	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	Y_{expt} (mean)	S_u^2	Y_{model}
1	1	- 1	- 1	0	1	0	0	1	1	0	91.53	0.125	91.25
2	1	- 1	1	0	-1	0	0	1	1	0	92.78	0.211	93.21
3	1	1	- 1	0	-1	0	0	1	1	0	90.93	0.245	91.25
4	1	1	1	0	1	0	0	1	1	0	93.68	4.50	93.21
5	1	- 1	0	- 1	0	1	0	1	0	1	92.13	0.583	92.29
6	1	- 1	0	1	0	-1	0	1	0	1	94.28	1.716	94.15
7	1	1	0	- 1	0	-1	0	1	0	1	92.53	2.00	92.29
8	1	1	0	1	0	1	0	1	0	1	94.18	0.50	94.15
9	1	0	- 1	- 1	0	0	1	0	1	1	90.65	0.145	90.55
10	1	0	- 1	1	0	0	-1	0	1	1	95.00	0.34	94.94
11	1	0	1	- 1	0	0	-1	0	1	1	95.10	0.231	95.04
12	1	0	1	1	0	0	1	0	1	1	94.39	0.627	94.37
13	1	0	0	0	0	0	0	0	0	0	95.20	0.845	94.7167
14	1	0	0	0	0	0	0	0	0	0	94.50	0.005	94.7167
15	1	0	0	0	0	0	0	0	0	0	95.40	0.627	94.7167
16	1	0	0	0	0	0	0	0	0	0	94.50	0.01	94.7167
17	1	0	0	0	0	0	0	0	0	0	93.00	0.500	94.7167
18	1	0	0	0	0	0	0	0	0	0	95.70	0.288	94.7167

Statistical Analysis and Response Surface Modeling

The coefficients of the obtained model for the Box – Behnken's RSM design are shown in Table 6 with the model equation given by equation 6.0. The linear, interaction and second order terms of the response model for the D – factor using the diagonal values of the Box – Behnken's inverted matrix are shown in Table 7. The entire linear terms coefficient whose absolute values are greater than or equal to 0.69 are significant. For the interaction terms, all coefficients whose absolute values are greater than or equal to 0.98 are significant while second order terms coefficients with absolute values greater than or equal to 0.93 are significant. The final model equation is given by equation 7.0 after eliminating the insignificant coefficients from the model equation. The adequacy of the model was done using Fisher's distribution table and adjudged to be adequate while the model accuracy was tested using the correlation coefficient, (R^2) which was found to be 0.8500. It was shown that the correlation between the input and output variables of the model is 85% accurate.

To show whether the correlation coefficient is significantly different from zero the Fisher's distribution table (F_R) was used to confirm it since the correlation coefficient is a random quantity which is adjudged to be significantly different from zero. It can be seen in table 6 that temperature and particle size has a significant effect on the dehydration of the ethanol – water mixtures which are synergistic.

Table 6 Summary of the Response Surface Model Coefficients

Linear Terms				Interaction Terms			Second Order Terms		
X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2
94.7167	0.0750	0.98	0.93	0.375	-0.125	-1.265	-1.4958	-0.9908	0.0592
$D_{LI} = 0.69$				$D_{IN} = 0.98$			$D_{Se} = 0.93$		

$$Y = 94.7167 + 0.0750X_1 + 0.98X_2 + 0.93X_3 + 0.375X_1X_2 - 0.125X_1X_3 - 1.265X_2X_3 - 1.4958X_1^2 - 0.9908X_2^2 + 0.0592X_3^2. \quad (6.0)$$

The final model equation after the elimination of the insignificant coefficients is given by equation 7.0.

$$Y_{model} = 94.7167 + 0.98X_2 + 0.93X_3 - 1.265X_2X_3 - 1.4958X_1^2 - 0.9908X_2^2 \quad (7.0)$$

Table 7 Values of Box – Behnken's Inverted Diagonal Matrix

A	C	d	e	g	P
0.1667	0.2292	-0.0208	0.1250	0.2500	-0.833

Optimization of the RSM Model

The response surface model was optimized using the Design expert (Design – Ease 8.03) software due to its user friendly nature over MATLAB in optimization. The function of desirability was employed since many solutions were predicted. The natural values of the experimental process variables with the highest desirability were selected as the optimum parameters for the dehydration of ethanol – water mixtures.

Table 8 Results of the Model Optimization

	X_1(Process duration (min)	X_2 (Particle size) (mm)	X_3 (Temperature) (°C)	Conversion (%)
Natural Variables	61.69	2.75	49.95	95.4065

Validation of the Optimum Conditions

The result of the optimization was validated by three replicated experiment with the obtained optimum result at the process variables predicted by the model.

Table 9 Result of the Optimization Validation

Y_1 (Response, %)	Y_2 (Response, %)	Y_3 (Response, %)	$Y_{average}$ (Response, %)
95.70	93.90	95.40	95.00

The result obtained from the experiment after three replications was 95.00%wt. while the model predicted optimum result is 95.4065%wt. The experimentally result obtained is 99.574% close to the result obtained from the predicted optimum value.

Table 10 Summary Results of the RSM Statistical Analysis

Parameters Tested	Test Used	Obtained Results	Remarks
Homogeneity of data	Cochran's test (G – test)	$G_{expt} = 0.33$ G_{table} (0.05,1,18) = 0.45	$G_{expt} < G_{table}$ Data is reproducible
Significant of the coefficients	Student's test (t – test) at 0.05 level of significance	1. Linear Terms ($D_{LI} = 0.69$) 2. Interaction terms ($D_{IN} = 0.98$) 3.Second order terms ($D_{Se} = 0.93$)	1. Absolute linear terms greater than or equal to 0.69 are significant. 2. Absolute values of interaction terms greater than or equal to 0.98 are significant 3. Absolute values of the second order terms greater than or equal to 0.93 are significant
Adequacy of the model	Fisher's test (F – test)	$F_{expt} = 0.61$ F_{table} (0.05,11,5) = 4.704	$F_{expt} < F_{table}$ (The model is adequate)
Model's Accuracy	Correlation coefficient, R^2	$R^2 = 0.8500$ R = 0.922	The model is adjudged accurate.
Correlation coefficient check, R	Fisher's test (F – test)	$F_R = 10.39$ F_{table}(0.05,11,5) = 4.704	$F_R > F_{table}$ (The correlation coefficient is significantly different from zero.

Response Surface Methodology Plots of the Model (3 – D)

The 3 – dimensional plot of the response surface model as depicted in figs. 1 – 6 shows that the optimum value of ethanol concentration obtained was around 95.5% wt. from an initial 90%wt. of ethanol –water concentration for the process variables studied. 96.5%wt. optimum ethanol concentration was obtained using sodium hydroxide as adsorbents by Ladisch and Dyck, (1979). Similar optimum value of ethanol concentration was obtained by Mya, (2011), using rice straw as adsorbents.

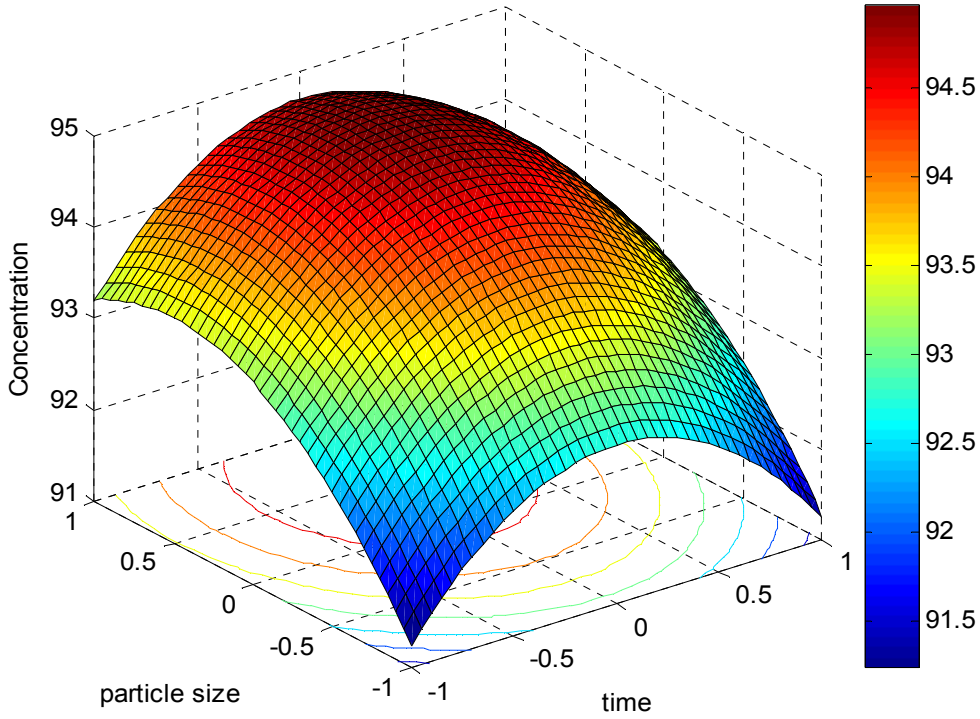

Fig. 1 3 – D plot of the process duration (time), particle size, and concentration

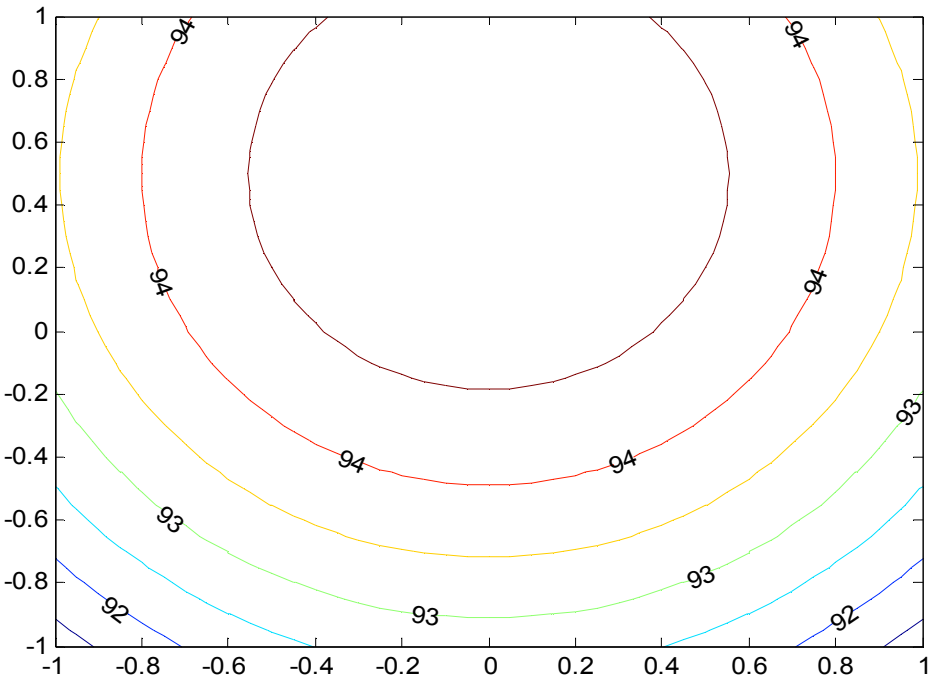

Fig. 2 Contour plot of the process duration, particle size, and concentration

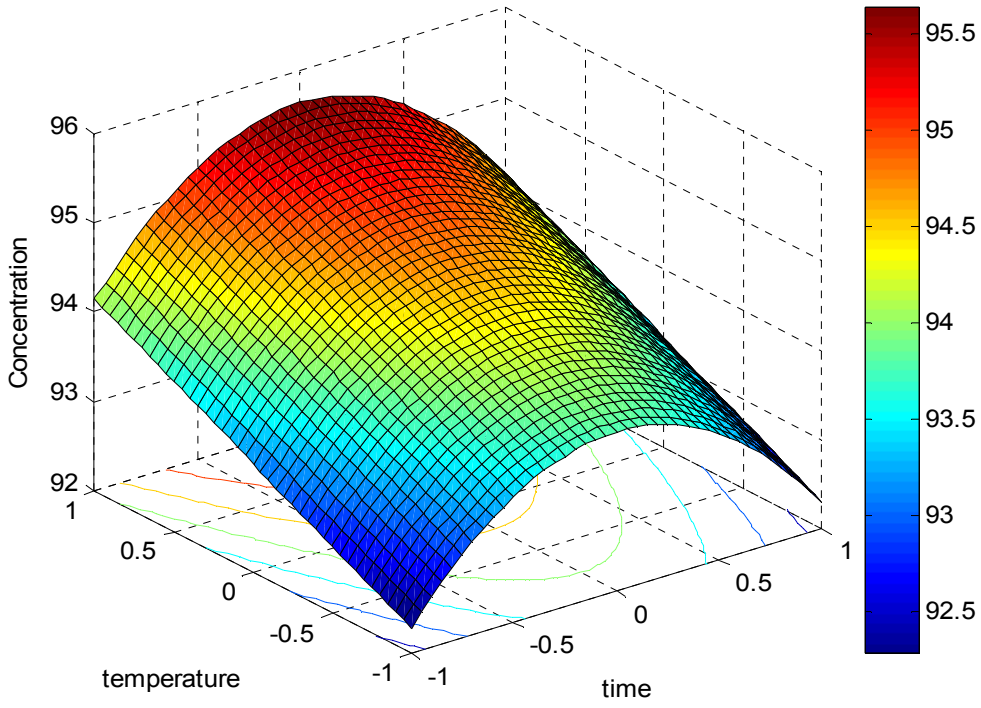

Fig. 3 3 – D plot of process duration (time), temperature, and concentration.

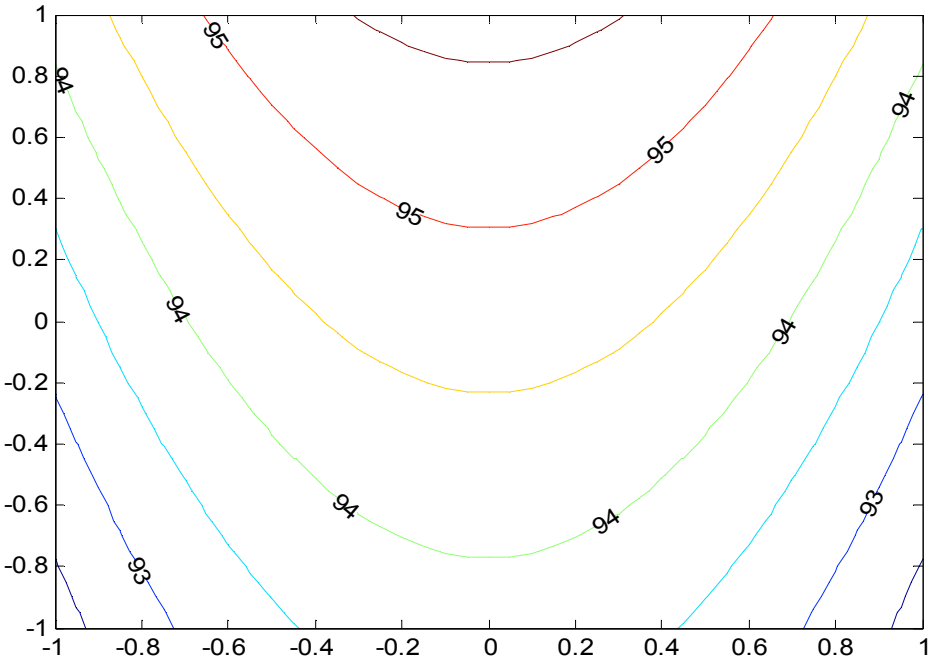

Fig. 4 Contour plot of process duration, temperature, and concentration.

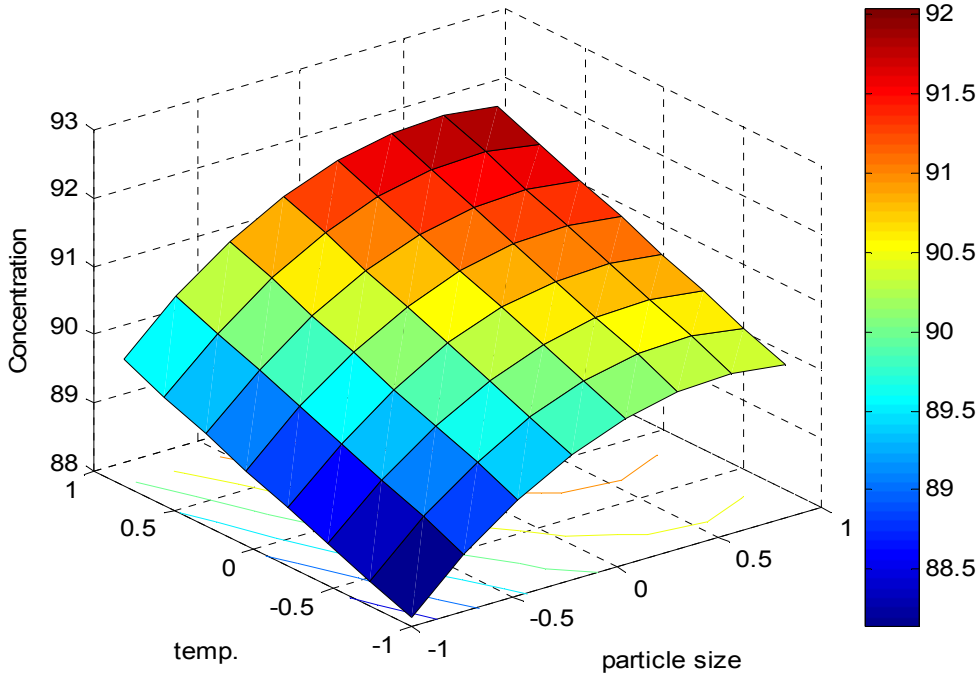

Fig. 5 3 – D plot of particle size, temperature, and concentration.

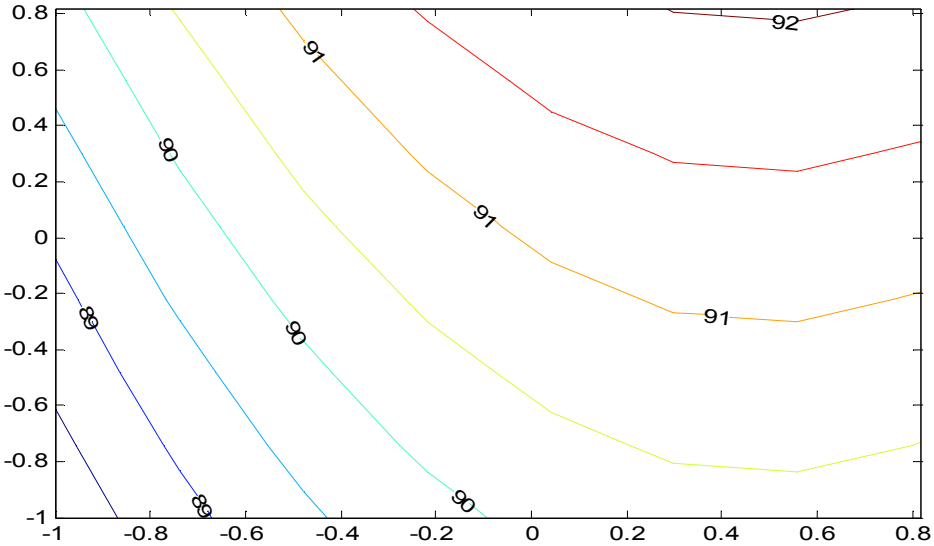

Fig. 6 Contour plot of particle size, temperature, and concentration.

X – Rays diffractogram analysis (X-RD)

Figure 7 is the X – RD pattern for the EMCOS. The strong X – ray diffractogram patterns of the enzyme modified corn starch noticed are; 14.664°, 17.212°, and 22.776° this corroborate the works of (Quintero and Cardona, 2009; Bertuzzi et al., 2007) which indicated a typical A type diffraction pattern. The amorphous zone present in the diffractogram is mainly due to amylopectin (Ahmad et al., 1999). Amylopectin α – 1, 6 branched structures has an overlapping hydroxyl groups which are proposed to correspond to more hydroxyl groups per unit area of the starch surface (Rebar et al., 1984). Thus, it was revealed that the dehydration noticed in enzyme modified corn starch was as a result of the amorphous nature of the biomass which resulted from the amylopectin structure as revealed in the X – RD analysis carried out on the biomass.

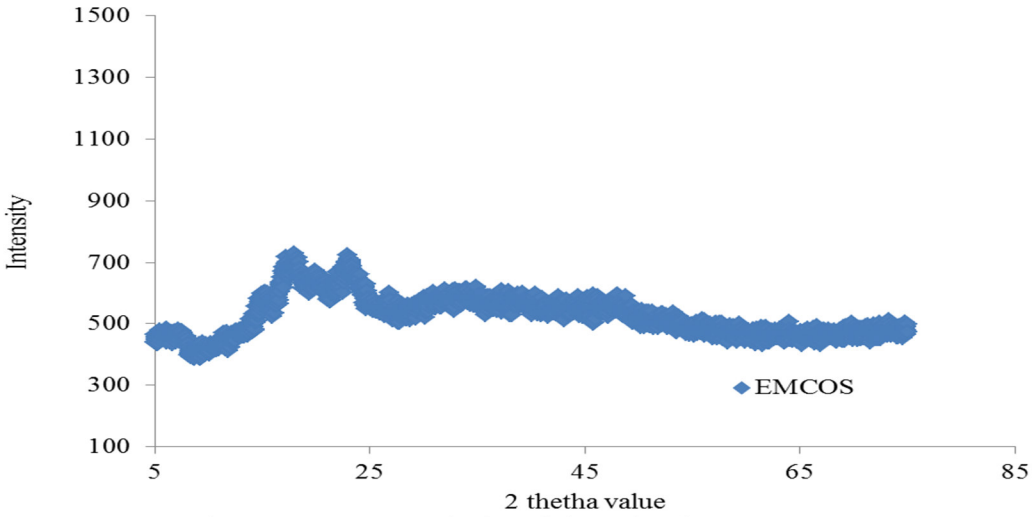

Fig. 7 X - RD analysis of the adsorbent

From figure 8 it was seen that the enzyme hydrolysis introduces characteristics pits and cracks as observed on the surface of the enzyme modified corn starch. The examinations showed that some regions of the granule are more susceptible to amylosis than others. Similar results were obtained by Sujka and Jamroz, (2006). The deepening of existing pores as well as creation of new ones can be attributed to the action of α – amylase enzyme. Hydrolysis occurred mainly in the more amorphous zones whereas crystalline were resistant to enzymatic action corroborating (Helbert et al., 1996; Planchot et al., 1995). The microscopic observations revealed the presence of pores on the surface of starch granules in conformity with results reported by Fannon et al., (1992). Corn starch granules are irregular in shape and their surface is uneven with numerous small depressions or pores with some granules completely smooth surface observed.

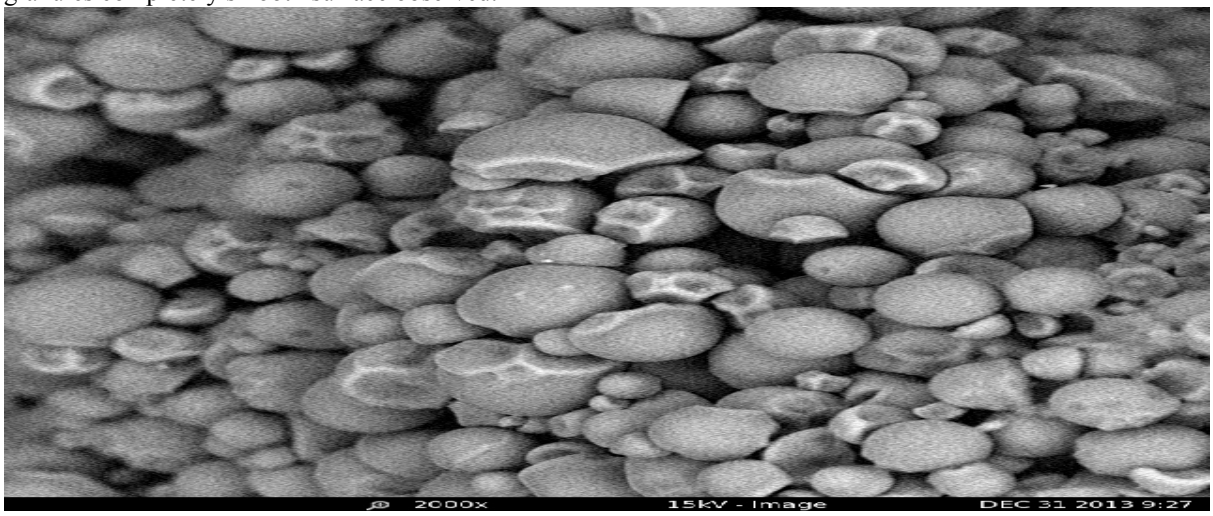

Fig. 8 Scanning electron microscopy for enzyme modified corn starch (EMCOS)

Conclusion

This work focussed on the response surface methodology optimization of the dehydration of ethanol – water mixtures using enzyme modified corn starch. A Box – Behnken design was used to design the experiment. The optimum concentration obtained was 95.4wt%. The results obtained from the validation agreed satisfactorily with the model predictions. The microscopic observations revealed the presence of pores on the surface of starch granules. It was revealed that the dehydration noticed in enzyme modified corn starch was as a result of the amorphous nature of the biomass which resulted from the amylopectin structure as revealed in the X – RD analysis carried out on the biomass.

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